

THE ABSORPTION SPECTRUM OF CHLORINE DIOXIDE
AND
INTENSITY DISTRIBUTION IN A BAND SYSTEM OF
SYMMETRICAL TRIATOMIC MOLECULES

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ZING WHAI KU

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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The Absorption Spectrum of Chlorine Dioxide

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The spectrum of the visible and ultraviolet absorption bands of ClO_2 has been studied under various dispersions. The band heads were measured with high precision. The result of the vibrational analysis shows that the bands may be represented by

$$\begin{aligned} \nu = & 20957.2 + 302.9(v_1' + \tfrac{1}{2}) - 2.3(v_1' + \tfrac{1}{2})^2 + 721.68(v_2' + \tfrac{1}{2}) \\ & - 2.797(v_2' + \tfrac{1}{2})^2 + 271.2(v_3' + \tfrac{1}{2}) \\ & - 4.42(v_1' + \tfrac{1}{2})(v_2' + \tfrac{1}{2}) - 3.9(v_1' + \tfrac{1}{2})(v_3' + \tfrac{1}{2}) \\ & - 5.9(v_2' + \tfrac{1}{2})(v_3' + \tfrac{1}{2}) - 529.0(v_1'' + \tfrac{1}{2}) \\ & - 1104.8(v_2'' + \tfrac{1}{2}) - 954.4(v_3'' + \tfrac{1}{2}) + 4.8(v_3'' + \tfrac{1}{2})^2, \end{aligned}$$

yielding three normal frequencies for each upper and lower electronic state. The essential difference between the present analysis and that of the previous investigators is discussed. Rotational lines are partially resolved on the plates taken in the second order with a 21-foot grating. Two fundamental and one combination bands in the region $4\text{--}11\mu$ were located with a self-recording spectrometer, and these are compared with the recent observation of Bailey and Cassie. Molecular constants have been calculated from a characteristic determinant given by Yates. They are found to be consistent with the observed isotope effect of chlorine.

THE absorption spectrum of chlorine dioxide has lately been studied by a number of investigators,^{1, 2, 3} but the work of Urey and Johnston has been the most extensive. They have measured the bands in the region $5042\text{--}3226\text{\AA}$. Their analysis of the vibrational structure yields three normal frequencies in the lower, and two in the upper electronic state. The observed intensity distribution has been found to be consistent with an extension of the Franck-Condon principle to polyatomic molecules.

Some time ago, as a preliminary for our study of intensity distribution in a band system of a triatomic molecule, the writer also examined the absorption spectrum of ClO_2 under various dispersions. In general, our measurements check well with those of Finkelnburg and Schumacher who photographed the spectrum with a two-meter grating, but they are more complete and extend into a higher frequency region. The rotational lines are partially resolved on our grating plates and reveal some interesting features. With a self-recording spectrometer,⁴ the fundamental and combination bands in the region 4 to 11μ

were found. Our observation has been confirmed by the recent work of Bailey and Cassie.⁵ It is the purpose of this paper to present our experimental results, to propose a new interpretation of the origin of the various progressions in the band system based on their relative intensities and the infrared data, and to deduce certain molecular constants from the results of the present analysis.

EXPERIMENTAL

As a source of illumination in the visible region, a Phillips lamp was employed with a glass or quartz spectrograph, and a 500-watt tungsten lamp with a grating spectrograph. In the ultraviolet region a water-cooled hydrogen discharge tube of the Bay and Steiner type,⁶ was used. Chlorine dioxide was prepared by reduction of Baker-analyzed potassium chlorate with oxalic crystals in the presence of a small amount of water as recommended by Bray.⁷ The gas was dried, fractionated, and frozen into crystals which could be kept for some time.

Two absorption cells of 20 cm and 1 meter length were made of Pyrex with fused quartz

¹ Goodeve and Stein, *Trans. Faraday Soc.* **25**, 738 (1929).

² Finkelnburg and Schumacher, *Zeits. f. physik. Chemie Bodenst.-Festband*, 704 (1931).

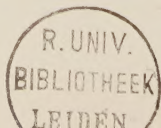
³ Urey and Johnston, *Phys. Rev.* **38**, 2131 (1931).

⁴ Randall and Strong, *Rev. Sci. Inst.* **2**, 585 (1931).

⁵ Bailey and Cassie, *Nature* **129**, 652 (1932). *Proc. Roy. Soc. A* **137**, 622 (1932).

⁶ Bay and Steiner, *Zeits. f. Physik* **45**, 337 (1927); **59**, 48 (1929).

⁷ Bray, *Zeits. f. physik. Chemie* **54**, 574 (1905).



plates cemented on both ends. The system was arranged for evacuation and circulation of the sample under observation. The pressure of the gas ranged from a few mm in the short cell to 1 atmosphere in the long cell. The best development of individual bands was found to be quite critical as to pressure, so it was not feasible to take a series of plates at once when working with the grating spectrograph.

The vibrational structure in the visible region was studied with the Michigan large glass spectrograph giving a dispersion of 9.0Å per mm at 5000Å, and in the ultraviolet region with a Hilger E1 quartz spectrograph. The rotational structure was photographed in the visible region with a 21-foot Rowland concave grating in a Paschen mounting giving a dispersion of 1.1Å per mm at 4600Å in the second order. Cramer's contrast and spectrum plates were used, and the time of exposure varied from fifteen to thirty minutes with a glass or quartz spectrograph, and two to four hours with a grating spectrograph. All the plates were taken at room temperature.

The plates were measured on a precision comparator. The wave-lengths were determined by comparison with the standard iron arc lines taken on the same plate. It is hoped that the wave numbers are correct within 1 cm^{-1} for the band heads. The precision of measurements for the bands with wave-length shorter than 3330Å was comparatively low because from there on the bands are no longer sharp and it was found difficult to make proper settings. The intensities were estimated by eye and checked with microphotometer records.

DESCRIPTION OF SPECTRUM

Fig. 1 is an enlarged reproduction of the spectrograms taken with a Hilger E1 spectrograph, and Fig. 2 is reprinted from the grating plates. An examination of the spectrograms reveals four or five well developed progressions indicated by the relative positions of the band heads, their intensities, and the similarity in the appearance of the rotational structure. The isotope effect of chlorine is prominent in certain bands, but ob-

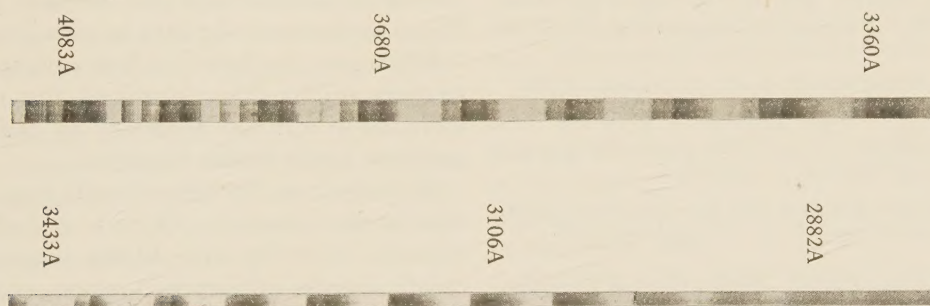


FIG. 1. Band system of ClO_2 .

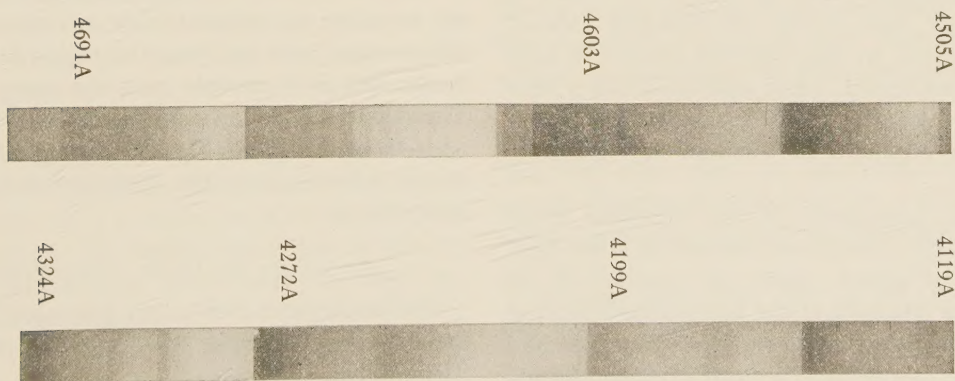


FIG. 2. Rotational structure of ClO_2 absorption bands.

TABLE I. Wave numbers in vacuum.

19,850.0	22,431.0	23,967.1	25,939.2	28,007.0	30,100	32,584
20,070.3	450.6	24,079.0	974.0	063.9	154	683
125.7	537.4	228.4	26,060.4	137.8	378	718
318.6	558.4	313.3	095.9	187.9	422	764
335.2	600.0	464.1	195.7	268.9	459	33,066
360.8	671.1	488.1	232.3	469.9	510	165
568.4	704.5	568.3	312.9	530.8	543	265
779.7	710.0	612.0	502.4	586.4	601	323
784.6	861.0	636.6	595.0	660.6	700	383
829.8	874.9	733.9	635.2	710.9	767	753
21,018.1	906.7	756.8	718.6	792.9	930	851
066.1	943.7	907.6	758.0	839.8	992	930
142.2	23,119.1	986.7	851.9	905.9	31,059	34,238
278.8	124.2	25,136.3	889.1	29,113.9	127	261
306.1	133.4	164.4	967.3	164.3	215	337
480.1	222.4	242.4	27,164.1	223.8	299	772
485.0	282.2	276.8	247.4	292.6	362	851
724.2	381.5	307.7	290.9	350.8	527	35,301
729.6	396.0	397.8	414.2	472.2	594	804
760.9	543.9	429.1	496.1	533.1	737	36,283
844.2	553.4	540.1	541.0	752.7	826	750
979.1	632.2	571.7	616.0	846.7	894	180
22,009.5	806.9	616.6	818.8	889.1	949	580
173.5	814.0	646.0	834.8	924.6	32,114	
177.7	900.0	836.0	893.6	980.6	183	
425.5	960.6	905.2	940.6	30,057.0	477	

scure in many others because of the high intensity near the band heads and the superposition of one band upon another. The relative intensity of various progressions and the isotope separation are seen in Fig. 3, which represents a part of the

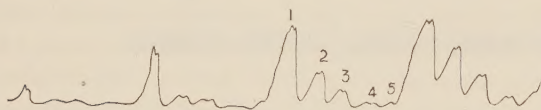


FIG. 3. 1. $(0, 8, 0) \leftarrow (0, 0, 0)$; 2. $(0, 9, 0) \leftarrow (1, 0, 0)$; 3. $(1, 8, 0) \leftarrow (0, 0, 0)$; 4. $(0, 10, 0) \leftarrow (0, 0, 1)$; 5. $(1, 8, 1) \leftarrow (0, 0, 0)$.

microphotometer records. The intensity of bands in each progression attains a maximum at about 3360Å and decreases uniformly on either side of the maximum. All bands lying below 3000Å fade away before their heads are reached. Several bands reported by the previous observers have not been confirmed, while additional ones have been found. In all we have measured 179 bands. The wave numbers in vacuum are given in Table I.

The great complexity of the rotational structure is evident. Each band consists of a few hundred lines of which many are unresolved. In general, the intensity of the band lines is highest near the head, decreasing rapidly toward the red till the lines merge into the head of a neighboring band. It is interesting to notice that in nearly all

the bands certain intense lines show up in groups at almost regular intervals on the wave-length scale. This feature is very prominent in the most intense progression and may be seen in Fig. 2. We have measured the lines in a few bands in the visible region, but have not been able to make an analysis. For further study of the rotational structure it will be necessary to examine the spectrum under higher dispersion.

Near infrared absorption bands were found to exist in three regions. There is a doublet with maxima at 10.78μ and 10.44μ respectively; a broad, intense absorption region extends between 9.26 – 8.88μ ; and a weaker band appears at 4.94μ . Weak absorption was also observed at 14.96μ and 4.28μ , but these are probably due to the presence of carbon dioxide as impurity. Two independent runs covering the region 1 – 19μ were made, and both records gave the same results.* The results of Bailey and Cassie⁵ are compared with these in Table II. The first half of each double column gives their measurements and the second ours.

ANALYSIS OF BAND STRUCTURE

The analysis of Urey and Johnston³ assumes the existence of three fundamental frequencies

* I should like to thank Professor W. W. Sleator for helping me to obtain these records.

TABLE II. *Infrared absorption bands.*

Band center (μ)	Maxima (cm^{-1})	Intensity	Identifica- tion†
14.96	668	weak	CO_2
10.57	932 928	20 medium	ν_3
	963 958		
9.017	1095 1080	50 intense	ν_1 ν_2
	1106		
	1123 1126		
5.307	1870	2	$2\nu_3$
	1884?		
	1900		
4.916	4.94 2034 2024	4 weak	$\nu_1 + \nu_3$ $\nu_2 + \nu_3$
	4.28 2336		
		weak	CO_2

† It should be pointed out that the assignment of ν_1 and ν_2 is quite arbitrary and an interchange of the subscripts introduces no change in the molecular constants.

which are not found in the infrared absorption. On the other hand, we are now quite sure that two of them are 1103 cm^{-1} and 943 cm^{-1} approximately, and we would expect them to be observable in the ultraviolet absorption. For according to the Boltzmann distribution law, molecules of a gas at ordinary temperatures will be present in appreciable numbers in all those higher states the energy of which does not differ from that of the lowest state by an amount of a higher order of magnitude than kT , while the majority of the molecules will be in the zero vibrational state. With the notation $(v_1', v_2', v_3') \leftarrow (v_1'', v_2'', v_3'')$ to represent a transition in absorption, and by taking the most intense v_2' progression to be $(0, v_2', 0) \leftarrow (0, 0, 0)$, we may look for those progressions originating from $(0, v_2', 0) \leftarrow (0, 1, 0)$ and $(0, v_2', 0) \leftarrow (0, 0, 1)$. These are found to be present. Among the bands in the long wavelength region a few members representing $(0, v_2', 0) \leftarrow (0, 0, 2)$ are also found. The third most intense v_2' progression may be regarded as arising from $(1, v_2', 0) \leftarrow (0, 0, 0)$. The assignment of bands to $(1, v_2', 0) \leftarrow (0, 0, 1)$ and $(1, v_2', 0) \leftarrow (0, 0, 2)$ then readily follows. We further note that of the remaining progressions three may be best accounted for as originating from the lowest level of the normal state to $(0, v_2', 0)$, $(1, v_2', 1)$, and $(2, v_2', 1)$ levels of the excited state. There remains but one well developed intense progression

which probably originates from a first vibrational level of the normal state with a vibrational energy 529 cm^{-1} . We shall, with the previous investigators, regard it as representing $(0, v_2', 0) \leftarrow (1, 0, 0)$.

If this assignment of the origin of these progressions be adopted, their relative quantum numbers are fixed. The bands are thus arranged in Table III. Up to $\nu = 30,378 \text{ cm}^{-1}$ all but a few bands are included.

It has been found that the measurements can be represented by the following expression:

$$\begin{aligned} \nu = & 20,957.2 + 302.9(v_1' + \tfrac{1}{2}) - 2.3(v_1' + \tfrac{1}{2})^2 \\ & + 721.68(v_2' + \tfrac{1}{2}) - 2.797(v_2' + \tfrac{1}{2})^2 \\ & + 271.2(v_3' + \tfrac{1}{2}) - 4.42(v_1' + \tfrac{1}{2})(v_2' + \tfrac{1}{2}) \\ & - 3.9(v_1' + \tfrac{1}{2})(v_3' + \tfrac{1}{2}) - 5.9(v_2' + \tfrac{1}{2})(v_3' + \tfrac{1}{2}) \\ & - 529.0(v_1'' + \tfrac{1}{2}) - 1104.8(v_2'' + \tfrac{1}{2}) \\ & - \begin{cases} 954.4 \\ 940.6 \end{cases} (v_3'' + \tfrac{1}{2}) + 4.8(v_3'' + \tfrac{1}{2})^2. \end{aligned}$$

This formula applies only to bands with v_2' equal to or less than 15. The members in the $(0, v_2', 0) \leftarrow (0, 0, 1)$ progression follow $\omega_3'' = 954.5$ for $v_2' \leq 7$ and $\omega_3'' = 940.6$ for $v_2' > 7$. The $\nu_{\text{obs.}} - \nu_{\text{calc.}}$ values are given in parentheses in Table III.

While several of these progressions extend far into the high frequency region no satisfactory formula has been obtained to represent this part of the spectrum. This is chiefly due to the irregularity in the $\omega_v : v^*$ relation. We shall return to this point later.

Knowing the three normal frequencies of vibration, we may proceed to calculate the force constants and the half-angle α at the apex of the triangular model XY_2 . On the assumption that the forces are central about each atom, Dennison has obtained a characteristic equation⁸ which enables us to express the force constants and the half-angle in terms of the frequencies of mechanical vibration of infinitesimal amplitudes. We find that with these two particular sets of observed frequencies his equation yields no consistent solutions. Yates,⁹ on the other hand, as-

* Mulliken (Rev. Mod. Phys. 2, 506 (1930)) defines $\Delta G(v + \tfrac{1}{2}) = G(v + 1) - G(v)$. It follows that $\omega_v = \tfrac{1}{2}[\Delta G(v + \tfrac{1}{2}) + \Delta G(v - \tfrac{1}{2})]$.

⁸ Dennison, Phil. Mag. 1, 195 (1926).

⁹ Yates, Phys. Rev. 36, 555 (1930).

TABLE III. Classification of bands. Values of $\nu_{\text{obs.}} - \nu_{\text{calc.}}$ are in parenthesis.

ν_2'	$\nu_3''=0$	$(0, \nu_2', 0) \leftarrow (0, 0, \nu_3'')$ 1	2	$\nu_3''=0$	$(1, \nu_2', 0) \leftarrow (0, 0, \nu_3'')$ 1	2
0	20318.6? (11.2)					
1	21018.1 (-0.2)	20070.3 (-3.2)	19134.1* (-4.2)	21306.1 (-1.9)	20360.8 (-2.4)	19424.4* (-3.6)
2	21724.2 (0.5)	20779.7 (0.8)	19841.7* (-2.0)	22009.5 (0.6)	21066.1 (2.0)	20125.7 (-3.2)
3	22425.5 (2.1)	21480.1 (1.5)	20542.3* (-1.1)	22704.5 (0.3)	21760.9 (1.5)	20829.8 (5.6)
4	23119.1 (1.6)	22173.5 (0.8)		23396.0 (2.1)	22450.6 (1.5)	
5	23806.9 (0.8)	22861.0 (-0.3)		24079.0 (0.9)	23133.4 (0.1)	
6	24488.1 (-0.9)	23543.9 (-0.3)		24756.8 (0.2)		
7	25164.4 (-2.0)	24228.4† (6.8)		25429.1 (-0.5)		
8	25836.0 (-2.2)	24907.6 (-0.6)		26095.9 (-1.0)		
9	26502.4 (-1.9)	25571.7 (-2.6)		26758.0 (-0.6)		
10	27164.1 (-0.8)	26232.3 (-2.6)		27414.2 (-0.6)		
11	27818.8 (-1.1)	26889.1 (-0.8)		28063.9 (-1.5)		
12	28469.9 (0.6)	27541.0 (1.7)		28710.9 (0.5)		
13	29113.9 (0.8)	28187.9 (4.8)		29350.8 (1.1)		
14	29752.7 (1.4)			29980.6 (-2.9)		
15	30377.6 (-6.3)			30601.2		

ν_2'	$(0, \nu_2', 1)$ $(0, 0, 0)$	$(0, \nu_2', 1)$ $(0, 0, 1)$	$(1, \nu_2', 1)$ $(0, 0, 0)$	$(2, \nu_2', 1)$ $(0, 0, 0)$	$(0, \nu_2', 0)$ $(1, 0, 0)$	$(0, \nu_2', 0)$ $(0, 1, 0)$
0	20568.4 (-5.3)	19625.4* (-3.5)		21142.2? (-7.3)		
1	21278.8 (0.1)	20335.2 (1.3)		21844.2 (-1.5)		
2	21979.1 (0.9)			22537.4 (1.1)		
3	22671.1 (-0.9)		22943.7? (-5.2)	23222.4 (1.1)		
4			23632.2 (-0.5)	23900.0 (-0.6)	22590.9 (2.4)	22009.5† (-3.2)
5			24313.3 (2.3)	24568.3 (-6.2)	23282.2 (5.1)	22704.5† (3.2)
6			24986.7 (3.1)	25242.4 (-0.3)	23960.6 (0.6)	23381.5 (-2.7)
7			25646.0 (-4.7)	25905.2 (-0.1)	24636.6 (-0.8)	24058.6* (-3.0)
8			26312.9 (0.8)	26549.5	25307.7 (-1.5)	24733.9 (0.5)
9			26967.3 (-0.6)		25974.0 (-1.3)	25397.8 (-1.7)
10			27616.0 (-2.2)		26635.2 (-0.7)	26060.4 (0.3)
11			28268.9 (6.0)		27290.9 (0.0)	26718.6 (3.5)
12			28905.9 (3.9)		27940.6 (0.3)	27368.6* (4.1)
13			29533.1 (-2.3)		28586.4 (2.3)	28007.0 (-1.3)
14			30154.2 (-9.1)		29223.8 (1.5)	
15					29846.7	

? Measured on one plate only.

* Measured by the previous observers.

† Coincidence with another band.

‡ Probably representing $(1, 6, 0) \leftarrow (1, 0, 0)$.

sumes that the force tending to restore a particle after a displacement is the sum of two types, the first acting along the line XY and obeying Hooke's law, the second, an angular restoring force acting at right angles to the first and proportional to the arc displacement of the Y 's. His expression is

$$\lambda - K'[1/m + 2 \sin^2 \alpha / M] = 0,$$

$$\lambda^2 - [(K' + 2k)/m + 2(K' \cos^2 \alpha + 2K \sin^2 \alpha)/M] \lambda + 2K'K(2/M + 1/m)/m = 0, \quad (1)$$

where K' and K are the force constants, m and M , the masses of the Y and X atoms respectively; α is the half-angle between the bonds and $\nu_i = \lambda_i^{1/2}/2\pi$, λ_i being the roots of Eqs. (1).

We have obtained two sets of solution for each electronic state. They are given in Table IV.

TABLE IV. $\omega(\text{cm}^{-1})$, $K(10^5 \text{ dynes per cm})$.

	Normal state		Excited state	
I	$\omega_1'' = 529$	$K' = 6.74$	$\omega_1' = 271.2$	$K' = 0.56$
	$\omega_2'' = 1105$	$K = 1.16$	$\omega_2' = 721.7$	$K = 1.56$
	$\omega_3'' = 954$	$\alpha = 32^\circ 30'$	$\omega_3' = 302.9$	$\alpha = 49^\circ 27'$
II	$\omega_1'' = 954$	$K' = 6.74$	$\omega_1' = 302.9$	$K' = 0.56$
	$\omega_2'' = 1105$	$K = 0.87$	$\omega_2' = 721.7$	$K = 1.56$
	$\omega_3'' = 529$	$\alpha = 60^\circ 40'$	$\omega_3' = 271.2$	$\alpha = 29^\circ 53'$

For the normal state, Bailey and Cassie⁵ applying Hund's idea of chemical binding¹⁰ and Dennison's investigation of an asymmetrical top molecule¹¹ consider the probable model to be an equilateral triangle, the length of the sides being approximately 1.2A. According to them the first

¹⁰ Hund, *Zeits. f. Physik* **73**, 1, 565 (1932).¹¹ Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

set of constants should be chosen. In obtaining this set of constants, we have assumed that the fundamental band 954 cm^{-1} corresponds to the unsymmetrical vibration ν_3 in which the electric moment oscillates along the axis of middle moment of inertia B , and hence there should be no zero branch. We assumed further that the fundamental band 1105 cm^{-1} is to be associated with a symmetrical vibration in which the electric moment oscillates along the axis of least moment of inertia A —in the present case, along the bisector of the angle between the bonds—and, therefore, a zero branch would be expected ($A/B \cong 0.8$). Now the envelopes of these bands appear to be in good accord with these characteristics. Thus we are led to the conclusion that the second set of constants is very improbable.

Now the doublet separation 30 cm^{-1} corresponds to a moment of inertia $52 \times 10^{-40}\text{ g cm}^2$. This value may be associated with either the least or the largest moment of inertia. In the first case, we obtain $1.84 \times 10^{-8}\text{ cm}$ for the distance between O—Cl; in the second case, $1.22 \times 10^{-8}\text{ cm}$. The model chosen ($\alpha = 32^\circ 30'$) is definitely in favor of the lower value.

In making a choice between the two sets of constants for the excited state, we shall turn to the theory of the isotope effect. Referring to Eqs. (1), we find that the calculated values of the isotope shift are somewhat too large compared with the observed values if the first set of constants (see Table IV) be used. On the other hand, from the second set we obtain a general agreement.

To a first approximation, the isotope shift is given by

$$\nu_2 - \nu_1 = \sum [(\rho_i' - 1)\omega_i'(v_i' + \frac{1}{2}) - (\rho_i'' - 1)\omega_i''(v_i'' + \frac{1}{2})],$$

where the subscripts 1 and 2 refer to the more and less abundant isotopes respectively, and ρ stands for the square root of the equivalent reduced masses, or $\rho = (\mu_1/\mu_2)^{\frac{1}{2}}$.

Using the second set of constants we obtain the following expressions for the isotope displacement:

$$(0, \nu_2', 0) \leftarrow (0, 0, 0), \quad \nu_2 - \nu_1 = 5.4 - 4.3\nu_2';$$

$$(1, \nu_2', 0) \leftarrow (0, 0, 0), \quad \nu_2 - \nu_1 = 3.1 - 4.3\nu_2';$$

$$(0, \nu_2', 0) \leftarrow (1, 0, 0), \quad \nu_2 - \nu_1 = 6.1 - 4.3\nu_2';$$

$$(0, \nu_2', 0) \leftarrow (0, 0, 1), \quad \nu_2 - \nu_1 = 10.6 - 4.3\nu_2'.$$

For the reasons already mentioned the isotope bands could be measured only with difficulty. In many cases the displacements turn out to be quite irregular; in others, our measurements do not check with those of previous observers. The observed and calculated values are compared in Table V. Perhaps without a knowledge of the band centers and the rotational structure a closer agreement can hardly be expected.

TABLE V. Isotope bands.

$(0, \nu_2', 0) \leftarrow (0, 0, 0)$		$(1, \nu_2', 0) \leftarrow (0, 0, 0)$		$(0, \nu_2', 0) \leftarrow (1, 0, 0)$		$(0, \nu_2', 0) \leftarrow (0, 0, 1)$	
ν_2'	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
4	-11.5*	-11.7	-14.5	-14.0			
5	-17.2*	-16.0	-20.4*	-18.3			
6	-24.0	-20.3	-22.9	-22.6	-22.4*	-19.6	
7	-28.1	-24.6	-31.3	-26.9	-24.6	-23.9	
8			-35.5	-31.2	-30.9	-28.2	
9			-38.3	-35.5	-34.8	-32.5	-31.6
10				-39.8	-40.2	-36.8	-36.6
11				-44.1	-43.5	-41.1	-37.2
12			-50.3	-48.4	-47.0	-45.4	-44.9
13				-52.7			-40.9
14			-56.0	-57.0			

* Measured by the previous observers.

Goodeve and Stein¹ have pointed out that there is a discontinuity in the curve when ω_v is plotted against v . The break in the curve occurs between $\nu_2' = 14$ and $\nu_2' = 15$, and has been accounted for as an indication of predissociation. From our measurements of the $(0, \nu_2', 0) \leftarrow (0, 0, 0)$ progression we have plotted this curve and is shown in Fig. 4. The curve is evidently nonlinear throughout its extent.

As has been pointed out by Birge¹² this feature is quite common with diatomic molecules, so

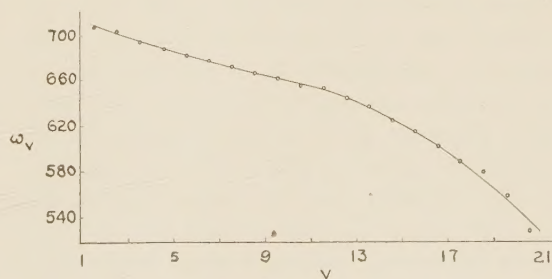


FIG. 4.

¹² Birge, Trans. Faraday Soc. 25, 707 (1931).

presumably it must also exist with more complicated ones. Unfortunately, we have not been able to trace the curve beyond $v=20$ with certainty, although we have measured 30 members in this progression and there is every indication that it extends far beyond the limit of observation. In view of this nonlinear relationship between ω_v and v , and the limited extent of our observation, any extrapolation to determine the heat of dissociation will be untrustworthy.

DISCUSSION OF RESULTS

It should be pointed out that the members forming the $(0, v_2', 0) \leftarrow (0, 0, 1)$ progression lie in regions where the $(1, v_2', 0) \leftarrow (1, 0, 0)$ progression should appear, and that the members representing the $(0, v_2', 0) \leftarrow (0, 1, 0)$ progression occupy the places where the isotope bands of the $(1, v_2', 0) \leftarrow (0, 0, 0)$ would be expected. This superposition effect very probably makes the intensity of these progressions higher than that estimated from the Boltzmann temperature factor $e^{-W/KT}$.

The present analysis yields three normal frequencies. There seems to be no obvious reason why no more bands forming a v_1' or v_3' progression

could be found. As has been pointed out in an early paragraph, the intensity in the most intense v_2' progression increases rapidly at first with the vibrational quantum number, reaches a maximum at about $v_2'=15$, and then decreases gradually. This most favored transition is connected with the change in the molecular configuration due to the electronic transition and is discussed in the following paper.

It is seen that the constants calculated from the electronic band spectrum data are in good agreement with the values deduced by Bailey and Cassie⁵ from the infrared band spectrum. This seems to support the results of the present analysis. However, in evaluating the molecular constants for the normal state we have assumed the existence of a fundamental band $\nu_1=529\text{ cm}^{-1}$ which has not been observed in the infrared absorption. This band, if it really exists, should lie approximately at 19μ which was the limit of our observation.

I wish to thank Professor D. M. Dennison for the guidance of this work, Professor W. F. Colby for helpful suggestions and discussions, and Professor R. A. Sawyer for kind help and advice during the course of experimentation.

Intensity Distribution in a Band System of Symmetrical Triatomic Molecules

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The Franck-Condon theory has been extended to a study of band intensities of a triatomic molecule of the general type XY_2 . The most probable transitions are found to be

$$\begin{aligned} v_1' &= \begin{cases} A_1 \pm B_1 v_1^{\frac{1}{2}} \pm C_1 v_2^{\frac{1}{2}} + D_1 v_1 + E_1 v_2 - F_1 v_1 - G_1 v_2 + H_1 (v_1 v_2)^{\frac{1}{2}} \\ A_1 \pm B_1 v_1^{\frac{1}{2}} \mp C_1 v_2^{\frac{1}{2}} + D_1 v_1 + E_1 v_2 - F_1 v_1 - G_1 v_2 - H_1 (v_1 v_2)^{\frac{1}{2}} \end{cases} \\ v_2' &= \begin{cases} A_2 \pm B_2 v_1^{\frac{1}{2}} \pm C_2 v_2^{\frac{1}{2}} + D_2 v_1 + E_2 v_2 - F_2 v_1 - G_2 v_2 + H_2 (v_1 v_2)^{\frac{1}{2}} \\ A_2 \pm B_2 v_1^{\frac{1}{2}} \mp C_2 v_2^{\frac{1}{2}} + D_2 v_1 + E_2 v_2 - F_2 v_1 - G_2 v_2 - H_2 (v_1 v_2)^{\frac{1}{2}} \end{cases} \\ v_3' &= \begin{cases} (\nu_3/\nu_3')v_3 \\ (\nu_3'/\nu_3)v_3 \end{cases} \end{aligned}$$

where the v 's with and without a prime refer to the vibrational quantum numbers of the upper and lower states, respectively, and the values of the coefficients depend on

the atomic masses, normal frequencies, force constants, and molecular dimensions. Two special cases which occur when the three atoms become equal and when the three atoms lie along a straight line are also considered. A wave mechanical treatment is outlined. It is found that for a triangular model the integrals, which measure the transition probabilities, corresponding to the $(v_3', 0)$ transitions when v_3' is an odd integer all vanish, and that for a linear model, in addition to these, all integrals pertaining to the $(v_2', 0)$ transitions when v_2' is an odd integer become zero. These results are, however, not to be interpreted as selection rules; they are simply consequences of the assumption of particular force fields. The results have been discussed in connection with the band intensities of ClO_2 . It is shown that a knowledge of the structure of the excited molecule is essential to test quantitatively the results of the present work.

INTRODUCTION

AS is well known, the relative intensities of bands in a band system are determined jointly by the initial distribution of molecules among the vibrational states and by the transition probabilities. The first factor depends, in emission, on experimental conditions such as temperature, pressure, mode of excitation, etc., and, in absorption, on the Boltzmann factor. In the following work we shall primarily be concerned with the transition probabilities in the absorption process at ordinary temperatures.

Based on Franck's theory of photochemical activity of molecules, Condon¹ has shown that the intensity distribution is definitely connected with the relative forms of $U'(r)$ and $U''(r)$ curves, and that in general there will be two or more most probable transitions for a given value of v' and v'' . He has also shown how the wave mechanics predicts the small but nonvanishing values of the transition probabilities outside the classical motion.

While many applications have been made to spectra of diatomic molecules, particularly absorption spectra, this principle has not as yet been applied in detail to polyatomic molecules. Recently Urey and Johnston² have found that the intensity distribution in the band system of ClO_2 satisfies qualitatively the Franck-Condon rule, but, as the writer has elsewhere³ pointed out, their analysis cannot be entirely correct and any improper correlation of the fundamental frequencies with the characteristic vibrations might vitiate their conclusions.

Despite our meager knowledge as regards the theory of electronic band spectra of polyatomic molecules and the actual forces that govern the nuclear motion of a complicated molecule, it might be of interest to question what sort of intensity distribution is to be expected from an extension of the Franck-Condon principle. In the present paper, we shall consider only molecules of the general type XY_2 and two special cases which occur when the three atoms are equal and when the three atoms lie along a straight line.

¹ Condon, *Phys. Rev.* **28**, 1182 (1926); *Proc. Nat. Acad. Sci.* **13**, 462 (1927); *Phys. Rev.* **32**, 858 (1928).

² Urey and Johnston, *Phys. Rev.* **38**, 2131 (1931).

³ The preceding paper, Ku, *Phys. Rev.* **44**, 376 (1933).

AN EXTENSION OF THE FRANCK-CONDON THEORY

For simplicity we shall assume that the atoms lie in a plane in the form of an isosceles triangle with the X atom at the apex. Let us introduce a set of coordinates q , x , y , and α to specify the molecular configuration, q being the relative displacement of the two Y atoms, x and y , the displacements of the X atom relative to the center of gravity of the Y atoms, and α the half angle at the apex of the isosceles triangle. To a first approximation, when the forces are assumed to be central about each atom* and the amplitudes of vibration are taken to be infinitesimal compared to the nuclear distances in equilibrium, the potential and kinetic energies expressed in the normal coordinates take the following simple form:

$$V = \frac{1}{2}(\lambda_1 \xi_1^2 + \lambda_2 \xi_2^2 + \lambda_3 \xi_3^2), \quad T = \frac{1}{2}(\dot{\xi}_1^2 + \dot{\xi}_2^2 + \dot{\xi}_3^2),$$

in which the ξ 's are obtained from the following transformation:

$$q = a_1 \xi_1 + a_2 \xi_2, \quad y = b_1 \xi_1 + b_2 \xi_2, \quad x = c \xi_3, \quad (1)$$

and the coefficients are given by

$$\begin{aligned} a_1 &= \frac{2}{m} \left(\frac{K + \frac{1}{2} K' \sin^2 \alpha - \frac{1}{2} m \lambda_2}{\lambda_1 - \lambda_2} \right)^{\frac{1}{2}}, & a_2 &= \frac{2}{m} \left(\frac{\frac{1}{2} m \lambda_1 - K - \frac{1}{2} K' \sin^2 \alpha}{\lambda_1 - \lambda_2} \right)^{\frac{1}{2}}, \\ b_1 &= -\frac{1}{m \mu^{\frac{1}{2}}} \left(\frac{\frac{1}{2} m \lambda_1 - K - \frac{1}{2} K' \sin^2 \alpha}{\lambda_1 - \lambda_2} \right)^{\frac{1}{2}}, & b_2 &= \frac{1}{m \mu^{\frac{1}{2}}} \left(\frac{K + \frac{1}{2} K' \sin^2 \alpha - \frac{1}{2} m \lambda_2}{\lambda_1 - \lambda_2} \right)^{\frac{1}{2}}, \\ c &= [2m\mu(1 + \mu \cot^2 \alpha)]^{-\frac{1}{2}}, \end{aligned}$$

where K and K' are the force constants, m and M the masses of the X and Y atoms, respectively, and λ 's the three roots of the characteristic determinant⁴

$$\left[\left(\frac{m\lambda}{K'} \right)^2 - 2 \left(\gamma + \frac{1}{2} + \frac{m}{M} \cos^2 \alpha \right) \frac{m\lambda}{K'} + \frac{2\gamma}{\mu} \cos^2 \alpha \right] \left[\frac{m\lambda}{K'} - 1 - \frac{2m}{M} \sin^2 \alpha \right] = 0,$$

where $\gamma = K/K'$, $\mu = M/(2m + M)$.

Evidently the vibratory motion of the system may be regarded as the motions of three independent equivalent harmonic oscillators with frequencies $\nu_i = \lambda_i^{\frac{1}{2}}/2\pi$. Now the motion of the i th simple harmonic oscillator expressed in the action and angle variables is given by

$$P_i = (2\mu_i \nu_i J_i)^{\frac{1}{2}} \cos 2\pi W_i, \quad \xi_i = (1/2\pi)(2J_i/\mu_i \nu_i)^{\frac{1}{2}} \sin 2\pi W_i.$$

⁴ Dennison, Phil. Mag. 1, 195 (1926).

* This restriction is in fact not necessary, for if we, with Yates⁵ assume that the force tending to restore a particle after a displacement is the sum of two types, the first acting along the line XY and obeying Hooke's law, the second, an angular restoring force, acting at right angles to the first and proportional to the arc displacement of the Y 's the characteristic determinant now takes the following form:

$$\left[\frac{\lambda m}{k'} - 1 - \frac{2m}{M} \sin^2 \alpha \right] \left[\left(\frac{\lambda m}{k'} \right)^2 - 2 \left(\frac{1}{2} + \frac{m}{M} \cos^2 \alpha + \frac{\gamma}{\mu} \sin^2 \alpha \right) \frac{\lambda m}{k'} + \frac{2\gamma}{\mu} \right] = 0$$

and the coefficients in Eqs. (1) become

$$\begin{aligned} a_1 &= \frac{2}{m} \left(\frac{K \cos^2 \alpha + \frac{1}{2} K' \sin^2 \alpha - \frac{1}{2} m \lambda_2}{\lambda_1 - \lambda_2} \right)^{\frac{1}{2}}, \\ a_2 &= \frac{2}{m} \left(\frac{\frac{1}{2} m \lambda_1 - K \cos^2 \alpha - \frac{1}{2} K' \sin^2 \alpha}{\lambda_1 - \lambda_2} \right)^{\frac{1}{2}}, \\ b_1 &= -\frac{1}{m \mu^{\frac{1}{2}}} \left(\frac{\frac{1}{2} m \lambda_1 - K \cos^2 \alpha - \frac{1}{2} K' \sin^2 \alpha}{\lambda_1 - \lambda_2} \right)^{\frac{1}{2}}, \\ b_2 &= \frac{1}{m \mu^{\frac{1}{2}}} \left(\frac{K \cos^2 \alpha + \frac{1}{2} K' \sin^2 \alpha - \frac{1}{2} m \lambda_2}{\lambda_1 - \lambda_2} \right)^{\frac{1}{2}}, \\ c &= \frac{1}{[2m\mu(1 + \mu \cot^2 \alpha)]^{\frac{1}{2}}}. \end{aligned}$$

⁵ Yates, Phys. Rev. 36, 555 (1930).

Following Condon we shall assume that the transition occurs instantaneously and that the motion of the massive nuclei is unaffected during the transition, then the following conditions must be satisfied:

$$q' = q'' + q_0, \quad y' = y'' + y_0, \quad x' = x'', \quad p_q' = p_q'', \quad p_y' = p_y'', \quad p_x' = p_x'',$$

where q_0 and y_0 denote the change in the nuclear distances of the normal configuration. Referring to Eqs. (1) we can immediately write down the following set of equations:

$$\frac{a_1'}{2\pi} \left(\frac{2J_1'}{\nu_1'} \right)^{\frac{1}{2}} \sin 2\pi W_1' + \frac{a_2'}{2\pi} \left(\frac{2J_2'}{\nu_2'} \right)^{\frac{1}{2}} \sin 2\pi W_2' = q_0 + \frac{a_1}{2\pi} \left(\frac{2J_1}{\nu_1} \right)^{\frac{1}{2}} \sin 2\pi W_1 + \frac{a_2}{2\pi} \left(\frac{2J_2}{\nu_2} \right)^{\frac{1}{2}} \sin 2\pi W_2,$$

$$a_1'(2\nu_1'J_1')^{\frac{1}{2}} \cos 2\pi W_1' + a_2'(2\nu_2'J_2')^{\frac{1}{2}} \cos 2\pi W_2' = a_1(2\nu_1J_1)^{\frac{1}{2}} \cos 2\pi W_1 + a_2(2\nu_2J_2)^{\frac{1}{2}} \cos 2\pi W_2, \text{ etc.,}$$

all double primes which refer to the lower state being dropped for the sake of convenience.* Solving for J_i' in terms of J_i and W_i by eliminating W_i' , writing θ_i for $2\pi W_i$ and replacing J_i by $\nu_i h$, we obtain

$$\begin{aligned} v_1' &= A_1 + B_1 \sin \theta_1 (\nu_1)^{\frac{1}{2}} + C_1 \sin \theta_2 (\nu_2)^{\frac{1}{2}} + D_1 \nu_1 + E_1 \nu_2 + F_1 \cos 2\theta_1 \nu_1 + G_1 \cos 2\theta_2 \nu_2 \\ &\quad + H_1 \sin \theta_1 \sin \theta_2 (\nu_1 \nu_2)^{\frac{1}{2}} + I_1 \cos \theta_1 \cos \theta_2 (\nu_1 \nu_2)^{\frac{1}{2}}, \\ v_2' &= A_2 + B_2 \sin \theta_1 (\nu_2)^{\frac{1}{2}} + C_2 \sin \theta_2 (\nu_2)^{\frac{1}{2}} + D_2 \nu_1 + E_2 \nu_2 + F_2 \cos 2\theta_2 \nu_2 + G_2 \cos 2\theta_1 \nu_1 \\ &\quad + H_2 \sin \theta_1 \sin \theta_2 (\nu_1 \nu_2)^{\frac{1}{2}} + I_2 \cos \theta_1 \cos \theta_2 (\nu_1 \nu_2)^{\frac{1}{2}}, \\ v_3' &= D_3 \nu_3 + F_3 \cos 2\theta_3 \nu_3, \end{aligned} \quad (2)$$

where

$$A_1 = (2\pi^2 \nu_1' / ha^2) (b_2' q_0 - a_2' y_0)^2, \quad A_2 = (2\pi^2 \nu_2' / ha^2) (b_1' q_0 - a_1' y_0)^2,$$

$$B_1 = (2/a^2) (b_2' q_0 - a_2' y_0) (a_1 b_2' - b_1 a_2') (2\pi^2 \nu_1'^2 / h \nu_1)^{\frac{1}{2}},$$

$$B_2 = (2/a^2) (b_1' q_0 - a_1' y_0) (a_2 b_1' - b_2 a_1') (2\pi^2 \nu_2'^2 / h \nu_2)^{\frac{1}{2}},$$

$$C_1 = (2/a^2) (b_2' q_0 - a_2' y_0) (a_2 b_2' - b_2 a_2') (2\pi^2 \nu_1'^2 / h \nu_2)^{\frac{1}{2}},$$

$$C_2 = (2/a^2) (b_1' q_0 - a_1' y_0) (a_2 b_1' - b_2 a_1') (2\pi^2 \nu_2'^2 / h \nu_2)^{\frac{1}{2}},$$

$$D_1 = (1/2a^2) (a_1 b_2' - b_1 a_2')^2 (\nu_1 / \nu_1' + \nu_1' / \nu_1),$$

$$D_2 = (1/2a^2) (a_1 b_1' - b_1 a_1')^2 (\nu_1 / \nu_2' + \nu_2' / \nu_1),$$

$$D_3 = \frac{1}{2} (\nu_3 / \nu_3' + \nu_3' / \nu_3),$$

$$E_1 = (1/2a^2) (a_2 b_2' - b_2 a_2')^2 (\nu_2 / \nu_1' + \nu_1' / \nu_2),$$

$$E_2 = (1/2a^2) (a_2 b_1' - b_2 a_1')^2 (\nu_2 / \nu_2' + \nu_2' / \nu_2),$$

$$F_1 = (1/2a^2) (a_1 b_2' - b_1 a_2')^2 (\nu_1 / \nu_1' - \nu_1' / \nu_1),$$

$$F_2 = (1/2a^2) (a_1 b_1' - b_1 a_1')^2 (\nu_1 / \nu_2' - \nu_2' / \nu_1),$$

$$F_3 = \frac{1}{2} (\nu_3 / \nu_3' - \nu_3' / \nu_3),$$

$$G_1 = (1/2a^2) (a_2 b_2' - b_2 a_2')^2 (\nu_2 / \nu_1' - \nu_1' / \nu_2),$$

$$G_2 = (1/2a^2) (a_2 b_1' - b_2 a_1')^2 (\nu_2 / \nu_2' - \nu_2' / \nu_2),$$

$$H_1 = (2/a^2) (a_1 b_2' - b_1 a_2') (a_2 b_2' - b_2 a_2') (\nu_1'^2 / \nu_1 \nu_2)^{\frac{1}{2}},$$

$$H_2 = (2/a^2) (a_1 b_1' - b_1 a_1') (a_2 b_1' - b_2 a_1') (\nu_2'^2 / \nu_1 \nu_2)^{\frac{1}{2}},$$

* For the same reason all double primes shall be omitted throughout the following discussion.

$$I_1 = (2/a^2)(a_1b_2' - b_1a_2')(a_2b_2' - b_2a_2')(\nu_1\nu_2/\nu_1'^2)^{\frac{1}{2}},$$

$$I_2 = (2/a^2)(a_1b_1' - b_1a_1')(a_2b_1' - b_2a_1')(\nu_1\nu_2/\nu_2'^2)^{\frac{1}{2}},$$

$$a^2 = (a_1'b_2' - a_2'b_1') = 1/m^2\mu.$$

Supposing the electronic transition to be independent of the phase of motion, it is easy to see that the values of v_i' corresponding to the small values of $\partial v_i/\partial \theta_i$ will be strongly weighted. Consequently, the most probable values of v_i' are obtained by substituting in Eqs. (2) the values of θ_i satisfying

$$\partial v_1'/\partial \theta_1 = \partial v_1'/\partial \theta_2 = \partial v_2'/\partial \theta_1 = \partial v_2'/\partial \theta_2 = \partial v_3'/\partial \theta_3 = 0.$$

We finally obtain

$$\begin{aligned} v_1' &= \begin{cases} A_1 \pm B_1(v_1)^{\frac{1}{2}} \pm C_1(v_2)^{\frac{1}{2}} + D_1v_1 + E_1v_2 - F_1v_1 - G_1v_2 + H_1(v_1v_2)^{\frac{1}{2}} \\ A_1 \pm B_1(v_1)^{\frac{1}{2}} \mp C_1(v_2)^{\frac{1}{2}} + D_1v_1 + E_1v_2 - F_1v_1 - G_1v_2 - H_1(v_1v_2)^{\frac{1}{2}} \end{cases} \\ v_2' &= \begin{cases} A_2 \pm B_2(v_1)^{\frac{1}{2}} \pm C_2(v_2)^{\frac{1}{2}} + D_2v_1 + E_2v_2 - F_2v_1 - G_2v_2 + H_2(v_1v_2)^{\frac{1}{2}} \\ A_2 \pm B_2(v_1)^{\frac{1}{2}} \mp C_2(v_2)^{\frac{1}{2}} + D_2v_1 + E_2v_2 - F_2v_1 - G_2v_2 - H_2(v_1v_2)^{\frac{1}{2}} \end{cases} \\ v_3' &= \begin{cases} (\nu_3/\nu_3')v_3 \\ (\nu_3'/\nu_3)v_3. \end{cases} \end{aligned} \quad (3)$$

We notice that there are, in general, four most probable values of v_1' and v_2' corresponding to any set of v_1 and v_2 . This interdependence is one of the consequences of the character of vibration, the coordinates q and y being functions of ξ_1 and ξ_2 . On the other hand, x is a function of ξ_3 alone and hence v_3' varies independently. We further notice that in the absorption process when $v_1 = v_2 = v_3 = 0$, Eqs. (3) are reduced to $v_1' = A_1$, $v_2' = A_2$, $v_3' = 0$. While the values of A_1 and A_2 are explicitly given on page 385, it is more convenient for later discussion to write

$$v_1' = \frac{1}{2}m^2\mu\alpha_1'(b_2'q_0 - a_2'y_0)^2, \quad v_2' = \frac{1}{2}m^2\mu\alpha_2'(b_1'q_0 - a_1'y_0)^2, \quad (4)$$

where

$$\alpha_1' = 4\pi^2\nu_1'/h, \quad \alpha_2' = 4\pi^2\nu_2'/h.$$

Here the α 's may be regarded as the amplitudes of the nuclear vibration in terms of the normal frequencies, and the a 's and b 's the amplitude of the component displacements of the nuclei. It has been found that there exists a simple relation between the most probable values of v_1' and v_2' given by

$$v_1'/\nu_1' + v_2'/\nu_2' = (2m/h)(q_0^2 + 4\mu y_0^2). \quad (5)$$

We may then conclude that in the absorption process at ordinary temperatures the strongest bands in the v_1' and v_2' progressions will be $(v_1', 0)$ and $(v_2', 0)$ where v_1' and v_2' are associated with the quantized states in the neighborhood of the unquantized ones determined by A_1 and A_2 . It is clear that if there be small change in the normal moment of inertia caused by the electron jump approaching the case $q_0 = y_0 = 0$, the most probable transitions would be the $(0, 0)$ bands. The strongest band in the v_3' progression is, however, always $(0, 0)$.

Consider a special case which occurs when the three atoms become equal. Referring to the characteristic determinant on page 384 we obtain

$$\nu_1 = (1/2\pi)(3K'/m)^{\frac{1}{2}}, \quad \nu_2 = \nu_3 = \nu_1/2^{\frac{1}{2}}.$$

The coefficients in Eqs. (1) now become

$$a_1 = a_2 = 1/m^{\frac{1}{2}}, \quad b_1 = b_2 = -(3/4m)^{\frac{1}{2}}, \quad c = (3/4m)^{\frac{1}{2}}.$$

The most probable transitions are found to be

$$v_i' = A_i \pm B_i(v_i)^{\frac{1}{2}} + (D_i - F_i)v_i, \quad \text{for } |B_i/(4F_i(v_i)^{\frac{1}{2}})| > 1,$$

and in addition to these

$$v_i' = A_i + B_i^2/8F_i + (D_i + F_i)v_i, \quad \text{for } |B_i/(4F_i(v_i)^{\frac{1}{2}})| < 1, \quad i=1, 2 \quad (6)$$

$$v_3' = \begin{cases} (\nu_3/\nu_3')v_3, \\ (\nu_3'/\nu_3)v_3, \end{cases}$$

where

$$\begin{aligned} A_1 &= (\pi^2 m \nu_1' / 18h) q_0^2, & A_2 &= (25\pi m \nu_2' / 18h) q_0^2, \\ B_1 &= (\pi/3)(2m/h\nu_1)^{\frac{1}{2}} \nu_1' q_0, & B_2 &= (5\pi/3)(2m/h\nu_2)^{\frac{1}{2}} \nu_2' q_0, \\ D_1 &= \frac{1}{2}(\nu_1/\nu_1' + \nu_1'/\nu_1), & D_2 &= \frac{1}{2}(\nu_2/\nu_2' + \nu_2'/\nu_2), \\ F_1 &= \frac{1}{2}(\nu_1/\nu_1' - \nu_1'/\nu_1), & F_2 &= \frac{1}{2}(\nu_2/\nu_2' - \nu_2'/\nu_2). \end{aligned}$$

The distinction between v_2' and v_3' vanishes because of the degeneracy.

The vibrations of a collinear model have been discussed fully by Dennison.⁶ The method of finding the transition probabilities are very much the same as has already been sketched above and need not be repeated here. We shall simply give the most probable values of the v 's as follows:

$$v_1' = a_1 + (b_1 - d_1)v_1 - c_1(v_1)^{\frac{1}{2}}, \quad \text{when } |c_1/(4d_1(v_1)^{\frac{1}{2}})| > 1,$$

and in addition to these

$$v_1' = a_1 + c_1/8d_1 + (b_1 + d_1)v_1, \quad \text{when } |c_1/(4d_1(v_1)^{\frac{1}{2}})| < 1,$$

where

$$\begin{aligned} a_1 &= (\pi^2 m \nu_1' / h) q_0^2, & b_1 &= \frac{1}{2}(\nu_1/\nu_1' + \nu_1'/\nu_1), \\ c_1 &= 2\pi \nu_1' (m/h\nu_1)^{\frac{1}{2}} q_0, & d_1 &= \frac{1}{2}(\nu_1/\nu_1' - \nu_1'/\nu_1); \\ v_2' &= \frac{1}{2}(\nu_2/\nu_2' + \nu_2'/\nu_2)v_2 \pm K(\nu_2/\nu_2' - \nu_2'/\nu_2); \end{aligned}$$

where K stands for $\cos 2\pi(\delta_z - \delta_y)$, δ_z and δ_y being the phase angle of the component harmonic vibrations of the isotropic plane oscillator. A special case occurs when the component harmonic vibrations are in phase ($\delta_z = \delta_y$), Eqs. (7) are reduced to

$$v_2' = \begin{cases} 3/2(\nu_2/\nu_2')v_2 \\ 3/2(\nu_2'/\nu_2)v_2; \end{cases} \quad v_3' = \begin{cases} (\nu_3/\nu_3')v_3 \\ (\nu_3'/\nu_3)v_3. \end{cases}$$

The above analysis leads to the following conclusions: In the absorption process at ordinary temperatures the most intense band in the v_1' progression will be $v_1' = a_1$; the larger the change in the normal equilibrium distance between the Y 's the higher will be the value of v_1' . The strongest band in the v_2' progression depends on the phase difference of the component harmonic vibrations as well as the characteristic frequencies in both states. The most intense band in the v_3' progression will again be (0, 0).

INTENSITY DISTRIBUTION ACCORDING TO WAVE MECHANICS

The same problem will now be considered from the wave mechanical standpoint. According to the usual method for calculating transition probabilities, the matrix component of the elec-

tric moment of the molecule corresponding to the transition in question must be computed. Born and Oppenheimer⁷ have shown how the general wave equation can be handled. On account of the heavy mass of the nuclei as compared with that of the electrons the complete wave function of a

⁶ Dennison, Rev. Mod. Phys. 3, 280 (1931).

⁷ Born and Oppenheimer, Ann. d. Physik 84, 457 (1927).

molecule in a state characterized by the electronic quantum number e and the vibrational quantum number v may be approximately written

$$\psi_{ev}(x, \xi) = \phi_e(x, \xi) u_{ev}(\xi),$$

where ϕ_e is the wave function of electronic motion, and u_{ev} is that of nuclear vibration, x and ξ being the collective coordinates of the electrons and nuclei respectively.

Since the nuclear motion of a symmetrical triatomic molecule may be resolved into that of three independent equivalent oscillators the vibrational factor of the wave function, to a first approximation, can be written

$$u_{ev}(\xi) = \Pi u_{ev}(\xi_i).$$

The electric moment $M(x, \xi)$ of the molecule is a linear function of the electronic and nuclear coordinates, and the matrix component of electric moment whose square measures the transition probability of an electronic transition (e' , e) and vibrational transition (v' , v) is

$$M \begin{pmatrix} e' & e \\ v' & v \end{pmatrix} = M(x, \xi) \psi_{e'v'}(x, \xi) \psi_{ev}(x, \xi) d\xi.$$

When studying the intensity distribution in a band system we shall deal with the same electronic transition. Suppose we integrate over the

electronic coordinates, then we have

$$M_{v'v} = M_{e'e}(\xi) u_{v'}(\xi) u_v(\xi) d\xi.$$

As ordinarily the wave functions vary with the nuclear coordinates much more rapidly than does the electric moment and the latter does not change very much over the region in which the wave functions have appreciable values, it becomes clear that for low values of v all but the constant term in $M_{e'e}(\xi)$ may be neglected. Writing $M_{e'e}(\xi) = A$ we have

$$M_{v'v} = A \Pi u_{v'}(\xi_i) u_v(\xi_i) d\xi_i.$$

If $u_{v_i'}(\xi_i) = (1/N_{v_i'}) H_{v_i'}(\eta_i') e^{-\eta_i'^2}$ is taken to be the wave function of the nuclear motion for the upper state,

$$u_{v_i}(\xi_i) = (1/N_{v_i}) H_{v_i}(\beta_i \eta_i' + \zeta_i) e^{-\frac{1}{2}(\beta_i \eta_i' + \zeta_i)^2}$$

then represents that for the lower state, where

$$\eta_i = \alpha_i^{\frac{1}{2}} \xi_i, \quad \alpha_i = 2\pi(\lambda_i)^{\frac{1}{2}}/h, \quad \beta_i = (\nu_i/\nu_i')^{\frac{1}{2}},$$

$$\zeta_i = \alpha_i^{\frac{1}{2}}(\xi_{ei}' - \xi_{ei}), \quad N_{v_i} = \pi^{\frac{1}{2}} 2^{v_i/2} (v_i!)^{\frac{1}{2}}$$

ξ_i being the normal coordinates of nuclei in the equilibrium configuration, H_{v_i} the Hermitian functions associated with the state specified.

The portion contributed by the i th oscillator will be

$$M_{v_i'v_i} = \frac{1}{N_{v_i'} N_{v_i}} \int H_{v_i'}(\eta_i') e^{-\eta_i'^2/2} H_{v_i}(\beta_i \eta_i' + \zeta_i) e^{-\frac{1}{2}(\beta_i \eta_i' + \zeta_i)^2} d\eta_i'. \quad (7)$$

If we study the absorption spectrum at a room temperature we shall primarily be interested in transition probabilities associated with bands originating from the lowest state, i.e., $v_i = 0$. For these transitions the integral may be evaluated quite easily. It may be shown that the matrix elements corresponding to the transitions (v_3' , 0) when v_3' is an odd integer all vanish, while all

others take on values depending on the ratio of the normal frequencies and molecular constants characteristic for the transition in question. The same statement holds for the case in which the three atoms become equal.

For a collinear model the integral which measures the transition probability is approximately

$$M_{v'v} = B \int u_{e'v'_1}(q) u_{ev_1}(q) u_{e'v'_2}(r, \phi) u_{ev_2}(r, \phi) u_{e'v'_3}(x) u_{ev_3}(x) dq dr d\phi dx,$$

where B is a constant representing the effective electric moment of the molecule for the electronic transition in question and

$$u_{v_1} = (1/N_{v_1}) H_{v_1}(\rho_1) e^{-\rho_1^2/2},$$

$$u_{v_2} = \rho_2^{|m|} \sum_{k=0}^{v_2-m} a_k \rho_2^k e^{-\rho_2^2/2} e^{im\phi},$$

$$u_{v_3} = (1/N_{v_3}) H_{v_3}(\rho_3) e^{-\rho_3^2/2},$$

$$\rho_1 = \pi(2m\nu_1/\hbar)^{1/2} q, \quad \rho_2 = 2\pi(\mu\nu_2/\hbar)^{1/2} r,$$

$$\rho_3 = 2\pi(\mu\nu_3/\hbar)^{1/2} x, \quad a_{k+2} = \frac{2k+2m-2v_2}{(k+2)(k+2m+2)} a_k.$$

It can be shown that the integrals corresponding to the transitions $(v_2', 0)$ or $(v_3', 0)$ when v_2' or v_3' is an odd integer all vanish and all other integrals may be expressed in terms of the normal frequencies and molecular constants.

Perhaps it should be emphasized that the vanishing of the matrix components representing transition probabilities as mentioned above is not to be interpreted as rigid selection rules. We have shown that on the assumption of any particular force fields—whether it be central or valence forces—we are led to deal with wave functions (e.g., Hermitian polynomials, functions containing a factor $e^{im\phi}$ where m is an integer positive or negative, etc.) whose properties are directly responsible for the vanishing integrals. As in an actual molecule, particularly when transitions to some high vibrational states are involved, the force fields might deviate considerably from what has been assumed, we would, therefore, rather expect some of the forbidden transitions to appear in the spectrum.

THE INTENSITIES OF THE ClO_2 BANDS

In the preceding paper³ we have mentioned the remarkable uniformity in the intensity distribution of the ClO_2 bands. In practically all the progressions there are central maxima which occur in the neighborhood of 3360Å. This general feature was reported by Urey and Johnston² who have plotted curves showing the distribution of intensities in the four most prominent v_2' progressions. The overlapping of bands makes the intensity measurement rather difficult. We have estimated the relative intensities from the micro-

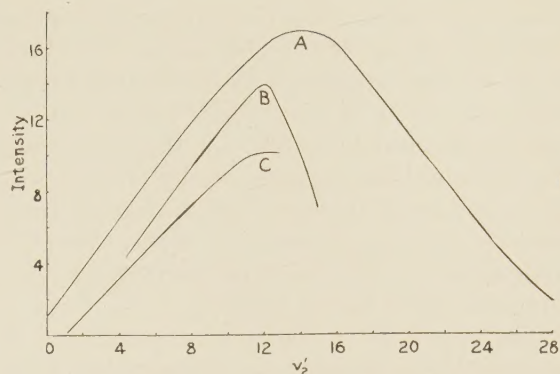


FIG. 1. A. $(0, v_2', 0) \leftarrow (0, 0, 0)$; B. $(0, v_2', 0) \leftarrow (1, 0, 0)$; C. $(0, v_2', 0) \leftarrow (0, 0, 1)$.

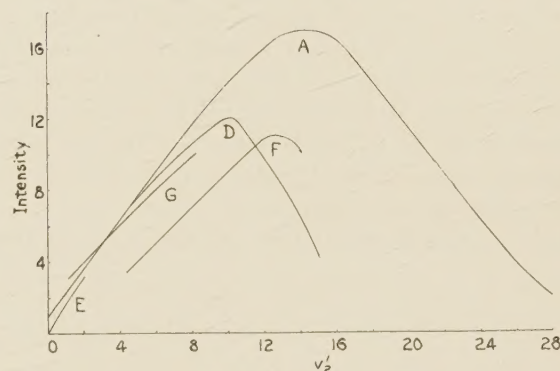


FIG. 2. A. $(0, v_2', 0) \leftarrow (0, 0, 0)$; D. $(1, v_2', 0) \leftarrow (0, 0, 0)$; E. $(0, v_2', 1) \leftarrow (0, 0, 0)$; F. $(1, v_2', 1) \leftarrow (0, 0, 0)$; G. $(2, v_2', 1) \leftarrow (0, 0, 0)$.

photometer records. These estimates have been made at points of maximum intensity in the unresolved bands and no corrections have been attempted for the variations of the dispersion of the instrument and of the plate sensitivity with the wave-length. The results are shown in Figs. 1 and 2 where the intensities in arbitrary unit are plotted against v_2' .

We are now ready to discuss how far the observed intensities agree with the results of the present analysis. On the whole, because of the Boltzmann factor, we would expect the bands originating from the $(0, 0, 0)$ level to be much stronger than the corresponding bands arising from any of the higher levels, and this has been found to be consistent with the vibrational analysis to which reference has been made. Let us assume, for the moment, our vibrational analysis to be correct and let us examine each mode of vibration independently. The absence of all bands associated with transitions to v_3' higher

than 1 and the fact that the corresponding members of (1, 0) are considerably weaker than those of (0, 0) seem to support the theoretical prediction that the (0, 0) transition in the (v_3' , 0) progression is most favorable. On the other hand, the nonvanishing intensity of the (1, 0) transition would mean that our wave mechanical treatment is inadequate and that higher orders of approximation must be employed in order to account for the observed intensity.

The intensities in the v_1' progression may be examined by comparing the corresponding members of (0, v_2' , 0) with those of (1, v_2' , 0) or (0, v_2' , 1) with (1, v_2' , 1), and (2, v_2' , 0), all originating from the ground state. Here too all transitions to v_1' higher than 2 are absent. We notice that, for $v_3'=0$, the corresponding members of the (1, 0) bands are much less intense than those of the (0, 0) bands; for $v_3'=1$, this becomes less obvious. The most probable value of v_1' therefore remains uncertain.

If we substitute in Eqs. (4) the value of the

molecular constants as given in Table V of the preceding paper we obtain

$$v_1' = 8.93 \times 10^{16} (1.25q_0 - 2.08y_0)^2,$$

$$v_2' = 23.8 \times 10^{16} (-1.44q_0 - 1.81y_0)^2.$$

With a knowledge of the most probable values of v_1 and v_2 it would seem possible to solve for q_0 and y_0 —the change in the nuclear distances in the normal equilibrium configuration—and consequently to calculate the dimensions of the excited molecule. We have seen in Fig. 1 that the most intense band in the (0, v_2 , 0) (0, 0, 0) progression is $v_2'=14$ or 15. Unfortunately the most probable value of v_1' is not precisely known. Until we have known the values of y_0 and q_0 we cannot make use of Eqs. (3)–(6) to test quantitatively the results of the present work.

I wish to express my gratitude to Professor D. M. Dennison for his continued interest in the work and frequent discussions throughout the investigation.

